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ULTRAFAST SPECTROSCOPIC INVESTIGATION OF SHOCK COMPRESSED GLYCIDYL AZIDE POLYMER AND NITROCELLULOSE FILMS

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Abstract. As a first experiment to observe the initial chemical reactions induced by sub-picosecond laser driven shocks in energetic materials, we have investigated thin films of glycidyl azide polymer (GAP) and nitrocellulose (NC). The GAP and NC films were spin coated onto thin film metal layers that had been vapor coated onto transparent substrates. Sub-picosecond laser pulses were used to launch planar shock waves through the metal layer and into the GAP and NC films. Time-resolved displacement measurements of both GAP and NC films suggest that shock-induced chemical reaction may be occurring. While the GAP film velocity falls as expected between that of the Al free surface and the particle velocity (using the free surface approximation), the displacement measurements in NC films yield velocities lower than the particle velocity. While data modeling discounting reaction has been unsuccessful, FTIR microscopy confirms the presence of unreacted GAP and NC in the shocked regions of the films.

INTRODUCTION

A full description of shock-induced chemical reactivity requires a microscopic and ultrafast (sub-picosecond) understanding of the interaction of a shock wave with the energetic material in question. The present experiments are initial steps toward the extraction of such information in HE thin film environments that are informative of not only the molecular but also the bulk behavior of energetics under shock loading. The ability to generate flat shocks by means of ultrafast laser pulses combined with spatial interferometry and various analytical tools is proving quite promising in our study of shock-induced chemistry. The experiments on thin films of NC and GAP presented here illustrate the initial strides that have been made in preparation, analysis, and shock loading of thin HE films.

SAMPLE PREPARATION

Our substrates consist of a 250 nm Al layer that is vapor coated onto standard borosilicate glass microscope cover slips of 100-150 μm thickness by CVI, Inc. The surface RMS deviation of these Al-coated substrates has been measured to be approximately 5 nm using atomic force microscopy (AFM). These metal-coated glass cover slips serve as the substrate for our spin-coating process in which 150-300 μL of a solution in methyl ethyl ketone, 2-pentanone, cyclobutanone, and n-butyl acetate ("magic solvent") of either GAP or NC (12.6% N) is dropped onto the center of an Al-coated cover slip and then spun for 25s at 2500 rpm.

Film thickness is varied by varying the concentration in "magic solvent" of the energetic polymer under study, yielding final NC or GAP thicknesses ranging from 50 nm to several microns. Film thickness is measured by means of a Filmetrics reflectance spectrometer, both at the center of the

sample and at several other points radiating outward toward the edge in order to get a sense of thickness distribution across the sample. Good samples exhibit less than a 10% deviation in thickness across the entire area.

The film surface is also measured using the AFM in order to determine the RMS roughness across surface areas as large as 80 μm x 80 μm . Typical samples exhibit a 10 nm dispersion in height and good samples exhibit less than half of this value. We have observed the tendency of such spun films of GAP to pool toward the center over long (hours, days) timescales, causing uneven dispersion of the GAP on Al and possible error in initial film thickness measurements. However, exposure of such films to 365 nm light for one hour after spinning encourages wetting, thus inhibiting this pooling and producing film thicknesses that remain even and constant for weeks. This exposure to 365 nm light has been found to cause a ~15% reduction in intensity of the azide band of the GAP film as measured by FTIR. However, as the azide absorption in GAP is particularly strong, this reduction does not pose a serious hindrance.

LASER SHOCK GENERATION

The apparatus used to generate the planar shocks in the GAP and NC films consists of a chirped pulse amplified Ti:Sapphire laser system (Spectra Physics) which produces 110 fs laser pulses at 800 nm with approximately 10 mJ per pulse at 10 Hz. These pulses are split so that ca. 500 μJ is directed at the borosilicate side of the target and focused to a nominal 75 μm spot size. These Gaussian incident laser pulses are reproducibly flattened to better than 0.7 nm RMS over the entire 75 μm spot size after passage through the borosilicate cover slip¹, allowing for planar shock generation into the Al/GAP and Al/NC systems. The aftermath of shock break out from a single laser shot driven into a BK7-Al-NC target is shown in Figure 1.

A relatively weak portion of the laser output is employed in spatial interferometric detection² of optical phase and reflectivity change due to the shock pulse, and is thus temporally correlated with the shock-generating pulse. The weak portion is itself split into two relatively equal beams, one of which is thus directed to the "front" (i.e., the NC or GAP) side of the target, probing a large (300 μm) spot size inclusive of

Figure 1. Aftermath of shock breakout in GAP on Al.

the "shocked" 75 μm spot. The other half of the weak beam is recombined with this probe both spatially and temporally after being appropriately delayed in order to generate a fringe pattern that forms the crux of our data analysis. Measurement of change in optical phase ($\Delta\phi$) with time can be converted to surface displacement (Δx) through the relation

$$\Delta x = \Delta\phi \lambda (4\pi n \cos(\theta))^{-1}$$

in which λ is the wavelength, n is the refractive index (of GAP or NC or of air in the case of bare Al), and θ is the half angle between the incident and reflected probe pulse³.

A small amount of the initial 800 nm beam is also diverted from the amplifier into an optical parametric amplifier (Spectra Physics OPA800) in order to generate (after sum-difference mixing) tunable infrared sub-picosecond light pulses. These pulses, when tuned, for example, to the azide transition of GAP (~2100 cm^{-1}) or to the O_2NO stretch of NC (~1625 cm^{-1}), form a spectroscopic diagnostic for probing the initial decomposition pathways taken by GAP or NC upon shock-induced reaction. As the infrared source is tunable, after establishing the initial shift or disappearance of a given band, bands that might be expected to arise due to subsequent formation of products or intermediates (e.g., a N_2 transition) can also be dialed in and probed in time.

The use of the infrared OPA, together with the temporal measurement of shock breakout, will allow for a fuller understanding of detonation chemistry than has been possible thus far. Using the OPA concomitantly

Figure 2. Al free surface velocity, particle velocity, and GAP surface displacement.

with shock displacement measurements, we are able to study shock-induced chemistry spectroscopically and with sub-picosecond resolution. The incorporation of the infrared probe(s) is currently a work-in-progress, and while data presented here will concentrate only on results from surface displacement measurements, it is important to see the current results in the matrix of the eventual incorporation of the spectroscopic probe.

SHOCK-COMPRESSED GAP FILMS

Surface displacement due to shock propagation through a BK7-Al-GAP target has been measured using our spatial interferometric technique described above. Figure 2 shows the change in displacement measured for such a target from the "front" (GAP) side (solid curves) in comparison with the change measured at the free surface of a pure Al target (dotted line) due to a planar shock driven by our pump laser. Included in this figure is a curve representing particle velocity (u_p) based on the free surface approximation. The target employed in the collection of these data is composed of an 880 nm layer of GAP over 250 nm of Al vapor coated onto a 100-150 μm thick borosilicate microscope cover slip.

It can be found from the figure that the slope of the initial displacement v. time signal for the GAP sample lies between that of the free Al surface and the particle velocity for the shocked free Al. This result is

Figure 3. FTIR microscopy in region of azide band for shocked (dotted) and unshocked (solid) GAP on Al.

sensible in consideration of the impedance mismatch between GAP ($\rho_0 = 1.3$) and Al ($\rho_0 = 2.8$). As the P-U Hugoniot of Al is steeper than that of GAP, the crossing point of the GAP Hugoniot with the reflected Hugoniot of Al (corresponding to the rarefaction wave from the free surface) is found to be between the Al particle and free surface velocities.

One can also find from the figure that the optical phase change (and correspondingly the displacement) seems to level off and even drop at later times (~ 30 ps after the initial rise). This surprising result may be indicative of chemical reactivity due to shock propagation through the GAP (shock pressures in GAP derived from velocity measurements yield pressures of up to 130 kbar). It has been postulated⁴ that the initial step in GAP decomposition involves the endothermic formation of an ionic species with a concomitant volume decrease of $\sim 20\%$, which would correspond well with experimental findings. Further, modeling using a simple nonreactive model is unable to reproduce the data, and our initial work with reactive models seems to promise more success.

FTIR microscopy, however, has shown minimal changes in the GAP azide intensity in the area through which our shock has propagated in comparison with the unshocked film (see Figure 3). This signature of non-reactivity, while seemingly contrary to our results from data modeling, would not be terribly surprising as the

Figure 4. NC displacement at 2 angles, Al free surface velocity, and Al particle velocity.

shock pressure in the GAP is presently only ~ 50 kbar. Thus while our optical phase measurements indicate that shock-initiated chemical reaction may indeed be occurring in our GAP thin films, we are presently working on increasing our shock pressure in order to unequivocally provide spectra from shock-induced chemistry of thin GAP films.

SHOCK-COMPRESSED NC FILMS

Experiments similar to those described for GAP have been done using a nitrocellulose layer of variable thickness on our Al-BK7 substrates. Figure 4 shows the change in optical phase for a NC thin film sample against the Al free surface velocity curve and a curve representing Al particle velocity. It is seen from the Figure that in the case of NC the initial phase change closely follows the particle velocity, which would indicate a more substantial “push back” (possibly indicative of reactivity) than has been found for GAP.

While FTIR microscopy has shown that NC is present in the regions through which our shocks have been launched, analysis of the velocity data is unsuccessful using a non-reactive model, and the decrease in displacement at longer times is likewise indicative of reactivity. It would be expected that the NC would react under milder loading conditions than would GAP, and one possible explanation reconciling our data analysis with the FTIR results would be that NC from the unshocked regions could “creep” into the

reacted hole on long time scales. This possibility is currently being investigated.

We have also fabricated samples in which a thin (50 nm) layer of Al has been coated on top of NC layers of variable (50-200 nm) thicknesses, forming BK7-Al-NC-Al samples. Recent investigations of the breakout times through these samples have been undertaken in light of past results through bare Al order to measure the shock velocity through the NC layer.

CONCLUSIONS AND FUTURE DIRECTIONS

These initial experiments are paving the way toward a microscopic understanding of shock-initiated chemistry on sub-picosecond timescales. Incorporating spatial interferometry with short pulse lasers, “fast” infrared spectroscopy, FTIR microscopy, AFM, and other analytical methods, we are building an exacting and multifaceted methodology by which shock-induced chemistry can be probed and understood. We are presently working on increasing our shock pressures to ensure reaction of our thin film samples by tailoring the shock profile of the impinging pulse. Such work has led us to the study of electron-phonon coupling in metals and of shock propagation through bare metals as foundational to our thin film work with high energetics. We are furthering our understanding of our microscopic sample systems through data modeling and through the incorporation of several complimentary analytical tools.

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⁴ L. L. Davis, private communication, June 2001.